



# Chemical degradation of fluorosulfonamide fuel cell membrane polymer model compounds



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## HIGHLIGHTS

- Aromatic trifluoromethyl sulfonamide model compounds were prepared and degraded.
- Mono-, di- and tri-substituted compounds were compared.
- The mono-substituted compound shows greater stability than the di-substituted species.
- Loss of perfluorinated sulfonamide side chains is an important pathway.
- Dimerization and aromatic ring hydroxylation are also degradation pathways.

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## ABSTRACT

The durability of a polymer electrolyte fuel cell membrane, along with high proton conductivity and mechanical performance is critical to the success of these energy conversion devices. Extending our work in perfluorinated membrane stability, aromatic trifluoromethyl sulfonamide model compounds were prepared, and their oxidative degradation was examined. The chemical structures for the models were based on mono-, di- and tri-perfluorinated sulfonamide modified phenyl rings. Durability of the model compounds was evaluated by exposure to hydroxyl radicals generated using Fenton reagent and UV irradiation of hydrogen peroxide. LC–MS results for the mono-substituted model compound indicate greater stability to radical oxidation than the di-substituted species; loss of perfluorinated sulfonamide side chains appears to be an important pathway, along with dimerization and aromatic ring hydroxylation. The tri-substituted model compound also shows loss of side chains, with the mono-substituted compound being a major oxidation product, along with a limited amount of hydroxylation and dimerization of the starting material.

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## 1. Introduction

Polymer electrolyte membrane (PEM) fuel cells have attracted significant attention as an alternative energy source that can deliver clean, secure and economic power in both stationary and transportation applications [1–5]. The polymer membrane is at the heart of a PEM fuel cell; it allows the transportation of protons, separates fuel from oxidant and maintains separation of the cathode and the anode layers; membrane failure therefore equates to cell death. Durability remains a major target for improvement in fuel cell systems, with numerous factors existent that can drive fuel cells through chemical, thermal and mechanical failure modes

[4,6–9]. A significant amount of research has been carried out in an effort to understand and address the design of novel membrane polymers, improving operation lifetimes, increasing conductivity of the membrane, advancing mechanical and thermal durability, and incorporating inorganic additives [10–13].

It is widely believed that hydrogen peroxide is generated and diffuses throughout operating fuel cells, with a commonly proposed mechanism postulated based on the reaction of hydrogen and adsorbed oxygen on the cathode [14]. Oxygen crossover from the cathode to the anode in the presence corrosion metal ions is also a potential source of hydroxyl and hydroperoxyl radicals that can oxidize and destroy the membrane [15]. Simulation of hydrogen peroxide-based radical formation can be achieved using Fenton's reagent or UV/H<sub>2</sub>O<sub>2</sub> degradation tests. The oxidation–reduction cyclic reaction of Fe(II)/Fe(III) in the Fenton test causes the formation of hydroxyl and hydroperoxyl radicals

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continuously [16]. The effectiveness of  $\text{H}_2\text{O}_2/\text{UV}$ , which produces 2 mol of radicals per mole of photolyzed hydrogen peroxide, has been demonstrated as well [17]. In addition to resistance against chemical and mechanical degradation, fuel cell membranes must exhibit relatively high proton conductivity, high selectivity to proton permeability, high electrical resistance, especially at elevated temperatures [18,19]. Recent studies have shown that perfluorosulfonamide polymers have potential for use in PEMFCs, exhibiting favorable mechanical and chemical properties at elevated temperatures, coupled with high proton conductivity [19–23]. Such materials possess  $-\text{CF}_3$  and  $-\text{SO}_2$  groups, which have strong electron withdrawing effects, leading to high acidity and facilitated proton conduction. Fluorocarbon moieties are generally considered to be oxidatively stable, because of their strong carbon–fluorine bonds [24].

In the present work, the chemical stability and degradation mechanisms of synthetic model compounds (Fig. 1) which mimic perfluorosulfonamide polymers, in the presence of hydroxyl radicals, will be examined. Because placing multiple trifluoromethyl sulfonamide chains on single aromatic rings within PEM polymers is of potential interest as a means of enhancing proton conductivity, the mono-, di-, and tri-substituted model compounds will be examined.

## 2. Experimental

Aromatic trifluoromethylsulfonamide ionomers, Fig. 1, were synthesized according to the method given below. M-SAMC refers to the mono-sulfonamide model compound; D-SAMC and T-SAMC refer to the di- and tri-sulfonamide model compounds respectively.

### 2.1. Preparation and characterizations of the ionomers model compounds

#### 2.1.1. Materials

Benzenesulfonyl chloride, benzene-1,3-disulfonyl chloride, benzene-1,3,5-trisulfonyl chloride and tri-fluoromethanesulfonamide (Aldrich); ferrous sulfate heptahydrate (99%), hydrogen peroxide solution ( $\text{H}_2\text{O}_2$ , 30% w/v) and LC–MS solvents (acetonitrile, DI water, formic acid, trifluoroacetic acid – all HPLC grade) (Fisher Scientific) were all used as received.

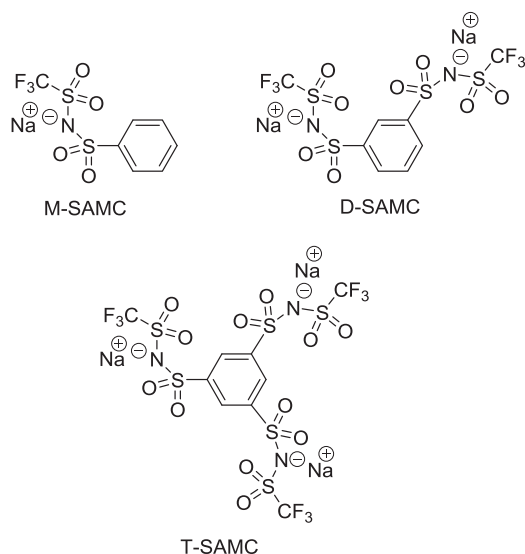


Fig. 1. Chemical structures of sulfonamide model compounds.

Triethylamine (Aldrich) was dried over potassium hydroxide and freshly distilled.

### 2.2. Characterization techniques

#### 2.2.1. Nuclear magnetic spectroscopy

$^1\text{H}$  NMR and  $^{19}\text{F}$  NMR were obtained at 600 MHz on Varian Inova Spectrometer VNMRJ 1.1D, software equipped with a Nalorac BB probe, at ambient temperature, dissolved in  $\text{D}_2\text{O}$  solvent, and internally referenced to TMS.

#### 2.2.2. Liquid chromatography mass spectrometry

Mass spectra were recorded on Thermo-LCF10166 LC–MS system, which is equipped with an HP/Agilent Zorbax column (Allure biphenyl column  $50 \times 2.1$  mm,  $5 \mu\text{m}$  particles size). Samples were injected onto the column using flow rate  $100 \mu\text{l min}^{-1}$ . The mobile phase used for gradient elution was acetonitrile/water containing 0.1% ammonium acetate. The solvent gradient started with (15:85 v/v) of water: acetonitrile for 2 min, then (30:70 v/v) of water: acetonitrile for 8 min. The column oven was maintained at  $60^\circ\text{C}$ . Ionization of analysts was performed using electrospray ionization (ESI) in the negative mode, focused on 100–1000  $m/z$ . A capillary temperature of  $257^\circ\text{C}$  was employed. Retention time (RT) and mass spectral details are reported herein.

#### 2.2.3. Synthesis and characterization of the model compounds

In a typical reaction, a solution of 0.35 g (2 mmol) benzenesulfonyl chloride in 2 ml anhydrous acetonitrile was slowly added to a cold (ice bath) solution of 0.3 g (2 mmol) trifluoromethanesulfonamide and 0.5 g (5 mmol) triethylamine in anhydrous acetonitrile. The reaction mixture was stirred for 2 h and allowed to warm up to room temperature and stirred for another 16 h. The mixture was washed with water and the product was extracted with chloroform. The organic layer was passed through an ion exchange membrane to obtain the product in the form of its sodium salt (95% yield), characterized by  $^1\text{H}$  and  $^{19}\text{F}$  NMR, and LC–MS.

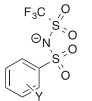
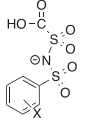
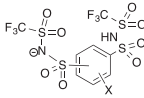
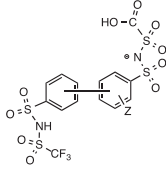
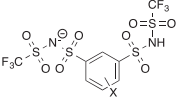
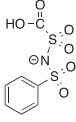
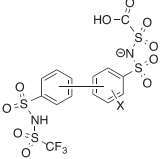
*N*-[(Trifluoromethyl)sulfonyl]benzenesulfonamide; M-SAMC m.p.  $56^\circ\text{C}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{D}_2\text{O}$ )  $\delta$  7.3 (s, 2H, aromatic),  $\delta$  7.4 (m, 2H, aromatic),  $\delta$  7.9 (s, 1H, aromatic).  $^{19}\text{F}$  NMR (600 MHz,  $\text{D}_2\text{O}$ )  $\delta$   $-79.06$  (3F, s). Mass (LCMS):  $m/z$  288 ( $\text{M}^+ - \text{Na}$ ). *N,N'*-bis[(trifluoromethyl)sulfonyl]benzene-1,3-disulfonamide; D-SAMC m.p.  $170^\circ\text{C}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{D}_2\text{O}$ )  $\delta$  7.6 (m, 1H, aromatic),  $\delta$  8.0 (s, 2H, aromatic),  $\delta$  8.3 (s, 1H, aromatic).  $^{19}\text{F}$  NMR (600 MHz,  $\text{D}_2\text{O}$ )  $\delta$   $-78.5$  (3F, s). Mass (LCMS):  $m/z$  499 ( $\text{M}^+ - \text{Na}$ ). *N,N',N''*-tris[(trifluoromethyl)sulfonyl]benzene-1,3,5-trisulfonamide; T-SAMC m.p.  $>250^\circ\text{C}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{D}_2\text{O}$ )  $\delta$  8.3 (s, 3H, aromatic).  $^{19}\text{F}$  NMR (600 MHz,  $\text{D}_2\text{O}$ )  $\delta$   $-79.11$  (3F, s) Mass (LCMS):  $m/z$  755 ( $\text{M}^+ - \text{Na}$ ).

### 2.3. Chemical degradation processes

#### 2.3.1. Degradation using Fenton's reagent

Fenton Reagent degradation was carried out by treating 10 mM solutions of the model compounds with 1.25 mM of ferrous sulfate. The mixture was purged using nitrogen gas for 10 min to avoid radical quenching that may occur in the presence of dissolved oxygen. 11 mM of  $\text{H}_2\text{O}_2$  was slowly added drop wise to accelerate the degradation reaction. The reaction solution was heated to  $70 \pm 2^\circ\text{C}$  and purged by nitrogen gas for 24 h. Another equal aliquot of ferrous sulfate was added to the mixture after 7 h. Approximately, 0.5 ml of the solution was taken after 1, 3, 5, 7 and 24 h to analyze for degradation using LC–MS.

**Table 1**  
Summary for products of degradation tests for model compounds.

Model Compound	Degradation test type	Resulted ions peaks m/z (Da)	RT (min)	Proposed compound
M-SAMC	Fenton, UV/H <sub>2</sub> O <sub>2</sub>	288	1.04	 Y=H
	Fenton	265	4.92	 X=2OH
	Fenton	297	4.92	X=2OH
	Fenton	499	0.55	 X=1OH
	Fenton	515	1.42	X=1OH
	Fenton	530	0.93	X=2OH
	UV/H <sub>2</sub> O <sub>2</sub>	304	0.42	Y=1OH
	UV/H <sub>2</sub> O <sub>2</sub>	320	0.36	Y=2OH
	UV/H <sub>2</sub> O <sub>2</sub>	599		 Z=3OH
	UV/H <sub>2</sub> O <sub>2</sub>	615	0.82	Z=4OH
	UV/H <sub>2</sub> O <sub>2</sub>	631		Z=5OH
	UV/H <sub>2</sub> O <sub>2</sub>	631		Z=5OH
D-SAMC	Fenton, UV/H <sub>2</sub> O <sub>2</sub>	499	0.55	 M-SAMC
	Fenton, UV/H <sub>2</sub> O <sub>2</sub>	288	1.04	X=1OH
	UV/H <sub>2</sub> O <sub>2</sub>	515	1.42	X=1OH
	Fenton	265	8.9	
	Fenton, UV/H <sub>2</sub> O <sub>2</sub>	614	1.0	
	Fenton, UV/H <sub>2</sub> O <sub>2</sub>	630	1.0	
	Fenton, UV/H <sub>2</sub> O <sub>2</sub>	645	1.0	

T-MSMC	Fenton, UV/H <sub>2</sub> O <sub>2</sub>	754			
	Fenton, UV/H <sub>2</sub> O <sub>2</sub>	732	2.26		
	Fenton, UV/H <sub>2</sub> O <sub>2</sub>	710			
	Fenton, UV/H <sub>2</sub> O <sub>2</sub>	355	1.73		
	Fenton, UV/H <sub>2</sub> O <sub>2</sub>	237	1.08		
	Fenton, UV/H <sub>2</sub> O <sub>2</sub>	288	1.04		
	Fenton	265			
			4.9		
	Fenton	297			
	UV/H <sub>2</sub> O <sub>2</sub>	623			
	UV/H <sub>2</sub> O <sub>2</sub>	601	1.59		
	UV/H <sub>2</sub> O <sub>2</sub>	597			
	Fenton	1477			
	Fenton	1433	2.40		
	Fenton	1412			

**[MNa<sub>2</sub><sup>-</sup>]**

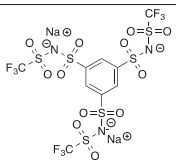
**[MHNa<sup>-</sup>]**

**[MH<sub>2</sub><sup>-</sup>]**

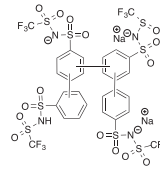
m/z, z=2

m/z, z=3

**M-SAMC**



**X=2OH**

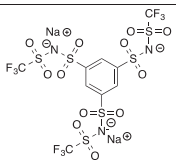


**[M<sub>4</sub>Na<sub>2</sub><sup>-</sup>]**

**[M<sub>4</sub>HNa<sup>-</sup>]**

**[M<sub>4</sub>H<sub>2</sub><sup>-</sup>]**

**X=OH**



**[M<sub>2</sub>H<sub>3</sub>Na<sub>2</sub><sup>-</sup>]-X**

**[M<sub>2</sub>H<sub>5</sub><sup>-</sup>]-X**

**[M<sub>2</sub><sup>-</sup>]**

### 2.3.2. Degradation using UV photolysis

10 mM solution of the model compounds were purged with dry nitrogen gas for 10 min, and then mixed with an equivalent concentration of H<sub>2</sub>O<sub>2</sub>. The light source was used is a 170 W mercury UV lamp (New Port ARC Lamp power supply model 69907), with intensity around  $500 \pm 40 \text{ mW cm}^{-2}$ , and a broad irradiation spectrum wave length range of 200–2500 nm. The solution was placed about 15 cm away from the light source; exposed to UV irradiation for an hour at room temperature with constant stirring.

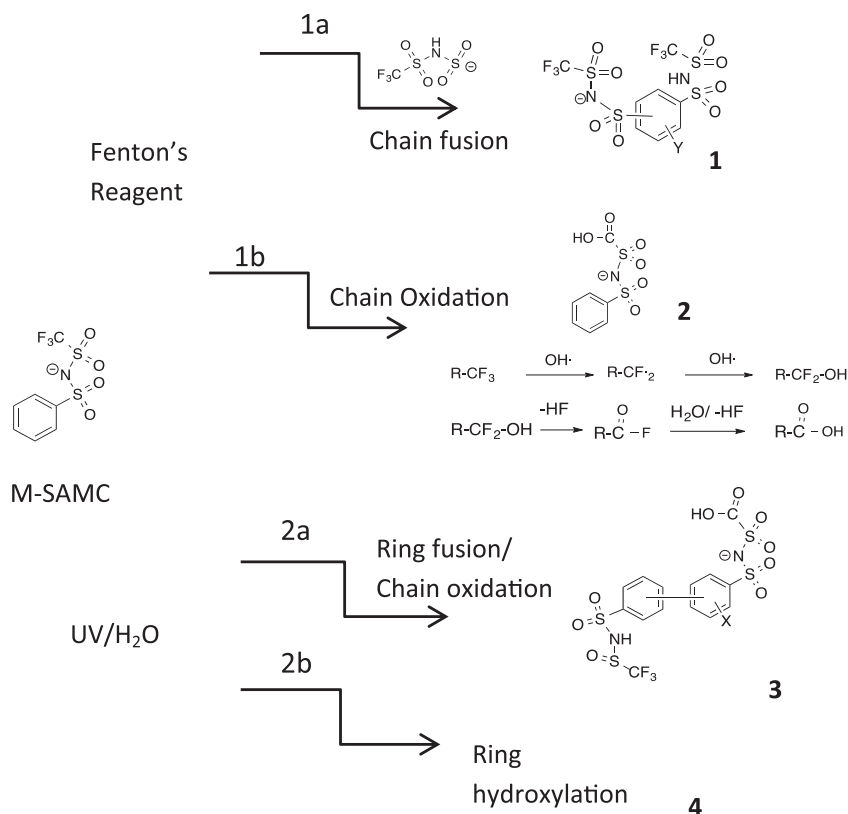
## 3. Result and discussion

The three model compounds (Fig. 1) were synthesized and characterized by NMR, then used for the oxidative degradation

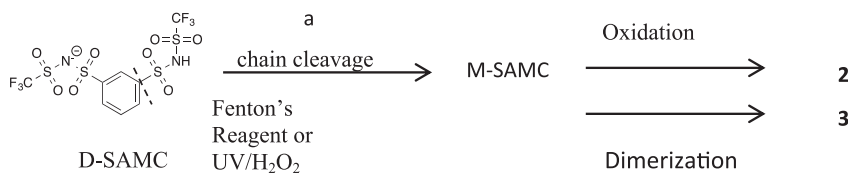
tests. Fenton's reagent and UV/H<sub>2</sub>O<sub>2</sub> oxidation processes offer two parallel methods, one metal-free, for delivering relatively high doses of radicals, allowing for accelerated lifetime testing of PEMFC materials [25]. Among these radicals, hydroxyl radical should be the most damaging species generated.

### 3.1. LC–MS data analysis

The use of the liquid chromatography/mass spectroscopy, equipped with electrospray ionization (ESI) detection in the negative ion mode, a soft ionization technique, was used because it causes little fragmentation, advantageous when high sensitivity molecular ion mass determination, and examination of polar compounds is required [26].



**Scheme 1.** Proposed degradation pathways of the M-SAMC using Fenton's reagent and UV/H<sub>2</sub>O<sub>2</sub>.



**Scheme 2.** Proposed pathways of the D-SAMC using Fenton reagent and UV/H<sub>2</sub>O<sub>2</sub>.

The model compounds (M-SAMC, D-SAMC, T-SAMC) represent a homologous series bearing varying numbers of the trifluoromethyl sulfonamide chains. Understanding of the effects of multiple sulfonamide chain substitutions upon oxidative stability of these materials is important as this determines the direction which associated PEMFC polymer synthetic efforts should follow. The LC–MS results of the degradation of the three model compounds after exposure to both Fenton's reagent and UV photolysis are presented [Table 1](#).

Previous studies have shown that the common products of Fenton or UV photolysis oxidation reactions of aromatic molecules are hydroxylated and dimerized products [27]. The hydroxyl radicals that are generated by those methods are thought to react with the phenyl ring, through a substitution, abstraction, or electron-transfer reaction. Addition of hydroxyl radical to produce an intermediate cyclohexadienyl radical could likely explain the observed products, and is more likely than simple atom abstraction; while direct fluorine atom abstraction is unlikely given the strength of C–F bonds, one cannot rule out electron transfer to the hydroxyl radical, followed by bond scission of the oxidized radical cation [27–30]. The present results show the molecular ion of the mono-substituted compound, M-SAMC at  $m/z = 288$  Da after losing

the Na<sup>+</sup> ion [M-SAMC – Cat<sup>+</sup>]<sup>–</sup>. The fragmentations have suggested two pathways for the model compound, [Scheme 1](#).

The product of path 1a, obtained in significant yield, exhibits MS peaks at 499 and 249 Da, which can be assigned to adduct formation as a result of fusion of a trifluoromethyl sulfonamide chain to the aromatic ring (compound **1**, YdbndH). The 249 peak would correspond to the doubly ionized species. Radical cleavage of the perfluoro side chains, followed by radical coupling would explain the formation of the disubstituted molecule starting from M-SAMC. As will be shown below, side chain cleavage is a fairly common event in these model compounds under hydroxy radical conditions. Further peaks were observed at  $m/z = 515$  and 530, which are attributed to the mono- and di-hydroxylated analogs of compound **1** in [Scheme 1](#). The major LC/MS peaks are summarized in [Table 1](#).

Conversion of model compound chain end group, –CF<sub>3</sub>, into –COOH during the degradation test is proposed to be the second Fenton test pathway shown in [Scheme 1](#). The proposed degradation mechanism, which is similar to the well-known attack of radicals on the poly (tetrafluoroethylene) backbones of Nafion<sup>®</sup> and other commercial PEM membrane polymers, begins with radical attack at the –CF<sub>3</sub> end chain group to form radical species R–CF<sub>2</sub>, which then captures a second hydroxyl radical to produce the R–CF<sub>2</sub>–OH

intermediate [5,10,31]. Elimination of HF would generate an acyl fluoride, which in the presence of water would hydrolyze to produce the carboxylic acid. Unlike the degradation of Nafion® chain ends, which are generally assumed to initiate from hydrogen atom abstractions (these hydrogens being present as a result of incomplete fluorination of the polymer), the current mechanism requires breaking of a more robust C–F bond. This difference could be the result of bond polarization in the very ionic model compounds, with or without electron transfer being the rate limited step in the process.

UV/H<sub>2</sub>O<sub>2</sub> photolysis could potentially open up different mechanistic pathways from those available during Fenton's oxidations, given the different concentration of radicals generated [32]. UV photo-oxidation resulted in a species which we attribute to the combination of fusion of two rings of the mono-model compounds, oxidation of one sulfonamide chain, and multiple ring hydroxylations; peaks observed at 599, 615, and 630 Da, which are attributed to tri, tetra, and penta hydroxylated products shown in Table 1. As illustration from the path 2b in Scheme 1, UV photolysis also produced a species with MS peaks at 304 and 320 Da, attributed here to direct hydroxylation of M-SAMC.

LC–MS analysis of the products resulting from Fenton's degradation of the bis-sulfonamide model compounds, bis[(trifluoromethyl)sulfonyl]benzene-1,3-disulfonamide (D-SAMC) gave rise to five separate species in significant concentrations. D-SAMC starting material exhibits its molecular ion of  $m/z = 499$  Da, compound minus sodium cation,  $[D-SAMC - Cat^+]^-$ , as well as its doubly charged ion peak resulting from loss of both sodiums  $[D-SAMC - 2Cat^+]^{2-}$ ,  $m/z = 249$  Da. The cleavage of trifluoromethyl sulfonamide chain from the model compound is a notable pathway under Fenton's oxidations; the fragment at 288 Da is proposed to be due to cleavage of a side chain/ring S–C bond, generating a product identical to the mono-substituted model compound. This result was further confirmed by <sup>19</sup>F NMR analysis; the M-SAMC exhibits a signal at –80.20 ppm corresponding to the fluorine atoms of the –CF<sub>3</sub> end group. The trifluoromethyl group D-SAMC spectrum is observed at –79.06 ppm. Fenton's degradation of the di-substituted model compounds shows NMR peaks for both the mono- and di-substituted compounds.

Side chain oxidation, and ring hydroxylation products were also apparent among the products of D-SAMC degradation – products similar to those obtained with M-SAMC oxidation were observed, Scheme 2. Additional products, corresponding to hydroxylation at four, five, six positions of the dimerized starting material where also observed with  $m/z$  values of 614, 630 and 645 Da, were observed; the analytical method cannot precisely identify the positions of these substitutions on the aromatic rings, nor whether dimerization or ring hydroxylation occurred first.

The UV/H<sub>2</sub>O<sub>2</sub> degradation test for D-SAMC model compound gave results very similar those obtained using Fenton's degradation conditions, Table 1.

LC–MS data for T-SAMC were recorded over the mass range 200–2000  $m/z$ . The parent peak of this model compound was observed at  $m/z = 754$  Da indicating presence of the molecule in its sodium salt form, along with loss of 2 and 3 cationic counter ions to give peaks at  $m/z$  355 and 237 Da respectively. Fenton's degradation of T-SAMC gave rise to less dimerization and hydroxylation products than were observed with its mono- and di-substituted analogs, perhaps in part due to steric crowding. A dimeric product, observed at 1477 Da, apparently monohydroxylated, was observed, Table 1.

Loss of two trifluoromethyl sulfonamide side chains, to produce M-SAMC, was also observed, at  $m/z$  288 Da, as were side chain oxidation and ring hydroxylations of the intermediate mono-substituted model compound. Similar products were observed using UV/H<sub>2</sub>O<sub>2</sub> oxidation of T-SAMC, and the presence of both

starting T-SAMC and M-SAMC (but not D-SAMC) was confirmed by <sup>19</sup>F NMR. Dimerized, mono-substituted products,  $m/z = 623$ , 601 and 579 were also observed as products of the UV/H<sub>2</sub>O<sub>2</sub> oxidation.

LC–MS results for M-SAMC have shown it to be more resistant to degradation than D-SAMC, as judged by the persistence of its  $m/z = 288$  Da, compared to that of the  $m/z = 499$  Da peak of the disubstituted model compound. The disubstituted molecule appears to readily lose a trifluoromethyl sulfonamide chain, followed by dimerization and hydroxylation. Insertion of a second perfluorinated sulfonamide chain on a phenyl ring used in PEMFC membranes appears to be a poor choice, based on oxidative stability. That same reaction path is observed in the trisubstituted model, T-SAMC. Both Fenton's and UV/H<sub>2</sub>O<sub>2</sub> degradations exhibit a peak at 288 Da, which is indicative of the single perfluorinated sulfonamide chain. i.e. 2 chains molecules have cleaved as a result of the degradation tests. The extent of this degradation pathway with T-SAMC, and the overall fewer fragmentations and the dimerizations observed in this system, suggest that it is more stable than D-SAMC in the presence of hydroxyl radicals, perhaps relating to the steric crowding in the presence of three substituent chains.

#### 4. Conclusions

Hydroxy radical oxidation of mono-, di-, and tri-substituted aromatic perfluorinated sulfonamide model compounds show all three molecules to be subject to degradation. LC–MS results for M-SAMC indicate that this material is more stable to radical oxidation than the di-substituted species, D-SAMC; the trisubstituted model compound is also more stable than the disubstituted material. Loss of perfluorinated sulfonamide side chains appears to be an important pathway, affecting all three model compounds, along with dimerization and hydroxylation of the aromatic rings. Oxidation of the terminal trifluoromethyl group on the side chains to produce a carboxylic acid, was observed as well. These results suggest that perfluorinated sulfonamides will exhibit chemical degradation much in the same manner as the perfluorinated ether polymers currently in use in PEM fuel cells.

#### Acknowledgments

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